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Active Sites for Methanol Dehydrogenation to Formaldehyde on Sodium-Modified Silicalite-1

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In order to elucidate active sites for selective dehydrogenation of methanol to formaldehyde on sodium-modified silicalite-1, adsorption of methanol on sodium-modified and -unmodified silicalite-1 has been investigated by a temperature-programmed desorption technique, infrared spectroscopy, and ab initio molecular orbital calculations. In sodium-modified silicalite-1, three kinds of the adsorption sites are present, that is, silanol sites, sodium-ion sites, and active oxygen bridge sites. Dissociative adsorption of methanol on the active oxygen bridge probably causes generation of silanol and methoxyl groups on the silicalite surface. By heating a sodium-modified silicalite-1 sample at 970 K, the number of the active oxygen bridges increased compared with that for the sample preheated at 770 K and its catalytic activity for methanol dehydrogenation also increased. Thus, it is proposed that methanol dehydrogenation is driven by the active oxygen bridges.

INTRODUCTION

Formaldehyde has been industrially produced by partial oxidation of methanol. The process has a disadvantage of the inevitable formation of water. Methanol dehydrogention to formaldehyde is an effective process because the products do not include water and also hydrogen is produced as a by-product. Catalysts containing transition-metal elements such as copper are very active toward alcohol dehydrogenation, but in the case of methanol dehydrogenation, carbon monoxide and hydrogen are mainly formed over these catalysts (*1*). Hence, the compounds that do not contain transition-metal elements are rather desirable for catalysts of methanol dehydrogenation to formaldehyde.

We have found that sodium-modified silicalite-1 catalyzes methanol dehydrogenation to formaldehyde (*2, 3*). It was confirmed that transition-metal elements as impurities do not function as main active sites and the catalytic activity depends on the amount of sodium ions in the silicalite sample (*3*). It is known that alcohol dehydrogenation proceeds over some basic catalysts (*4–8*). However, a basic property is not generated by modification of sodium ions on silicalite-1 (*9, 10*). Moreover, sodium ions do not function as Lewis acid (*10*); hence, it is implied that sodium ions are not reactive. Silicalite-1 also catalyzes ethanol dehydrogenation (*11*). In this case, the active sites are probably the Si–O–Si oxygen bridges generated by dehydration of the internal hydroxyl groups as structural defects (hydroxyl nests) in silicalite-1 (*11, 12*). It was confirmed that dissociative adsorption of ethanol proceeds on these oxygen bridges, hydroxyl and ethoxyl groups are generated, and the catalytic activity relates the number of ethanol adsorbed (*11*). Thus, it can be expected that methanol is also chemisorbed on the defect oxygen bridge and is transformed into formaldehyde. However, in the case of ethanol dehydrogenation, the catalytic activity does not depend on the number of sodium ions in silicalite-1 but only on the number of the

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active oxygen bridges (*11*). Hence, we need to confirm whether the oxygen bridges are active sites of methanol dehydrogenation. In the present work, methanol adsorption on sodium-modified and -unmodified silicalites was mainly investigated, and the active sites of methanol dehydrogention were studied.

EXPERIMENTAL

Materials

The preparation of sodium-modified silicalite-1 is described elsewhere (*3*). The sample (Na–SL) contained 1.2 wt% of sodium ions and its Si/Al molar ratio is ca. 4000. Electron microscopy indicated that the silicalite particles were spherical agglomerates, approximately 3–5 μm in diameter, made up of smaller crystals. By leaching sodium ions from Na–SL into boiling water three times for 5 h each, a sample containing 0.03 wt% of sodium ions (SL) was prepared. The XRD patterns of these samples preheated at 770–970 K are in agreement with those reported by Olson *et al.* (*13*). The XRD peaks were sharp, with no amorphous background, and no peaks other than those due to silicalite-1 were observed. The adsorption volume of the samples were measured by the adsorption of methanol at room temperature. The adsorption volumes were 0.16 ml g^{-1} for Na–SL heated at 770 K and 0.17 ml g^{-1} for SL heated at 770 K. The adsorption volumes did not change significantly after the samples were heated at 970 K.

Methanol was dried and distilled over 4A molecular sieves. Perdeuteromethanol (99.7% purity) was supplied by E. Merck AG. and used without further purification.

Temperature-Programmed Desorption

Temperature-programmed desorption (TPD) of methanol was conducted with a conventional apparatus equipped with a thermal conductivity detector. After heating at 770 K for 1 h or 970 K for 0.5 h *in vacuo*, the samples (0.100 g) were exposed to methanol vapor (1.3 kPa) at 390 K for 0.5 h and evacuated at room temperature for 1 h. TPD measurement was carried out from room temperature to 770 K with a heating rate of 10 K min^{-1} and with helium as carrier gas (flow rate, 20 ml min^{-1}).

Infrared Spectroscopy

Infrared spectra were recorded with a Nicolet 5DX FTIR spectrometer. The sample (0.01 g of Na–SL) was pressed into a self-supporting wafer and placed into an *in situ* IR cell allowing heating under vacuum. The sample was heated *in vacuo* at 970 K for 0.5 h. For recording IR spectra of adsorbed CD_3OD at room temperature, CD_3OD vapor (1.3 kPa) was contacted with the sample at 390 K and evacuated at a desired temperature for 1 h.

Methanol Conversion

Reactions were carried out in a fixed-bed continuous flow reactor. After a catalyst (0.050 g) was heated at 770 K for 1 h or at 970 K for 0.5 h under helium stream, methanol was fed via the helium stream (20 ml min^{-1}) to the catalyst bed at 720 K. The reaction was carried out at atmospheric pressure and partial pressure of methanol was 1.6 kPa.

RESULTS

TPD of Methanol

As shown in Fig. 1a and 1b, the TPD profiles of methanol for SL showed small and broad desorption peaks. The range of peaks in the profile for SL preheated at 770 K (a) can be deconvoluted into two peaks, i.e., the peaks at ca. 370 K (A-peak) and at ca. 470 K (C-peak). The peaks were approximated by using the Lorentz functions. In the case of SL preheated at 970 K (b), the range of peaks can also be deconvoluted into two peaks and the temperatures at peak maxima of these peaks are similar to those observed in profile (a) with the minor difference being that A-peak in profile (b) is smaller and C-peak is larger than those in profile (a). The amount of methanol adsorbed on SL preheated at 770 K or 970 K was ca. 0.1 mmol g^{-1} determined from the TPD profiles.

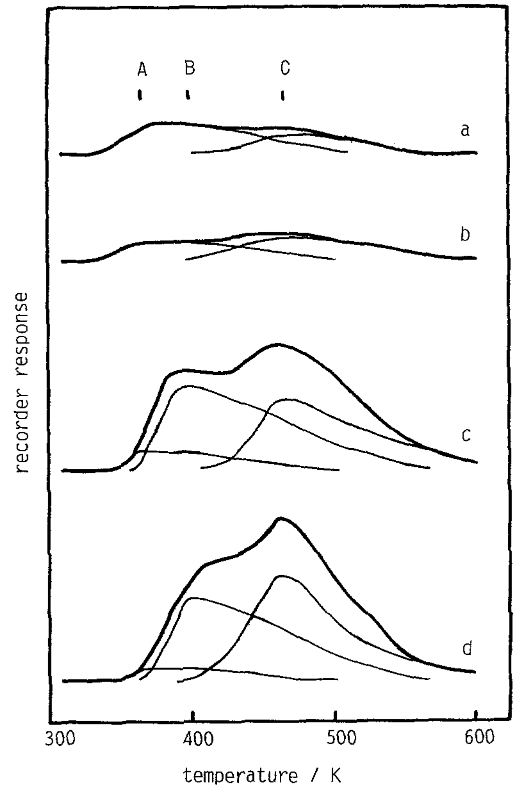

FIG. 1. TPD profiles of methanol from SL and Na–SL. (a) SL, 770 K; (b) SL, 970 K; (c) Na–SL, 770 K; (d) Na–SL, 970 K.

On the other hand, broad and large desorption peaks were observed in the TPD profiles for Na–SL. The amount of methanol adsorbed was ca. 0.4 mmol g^{-1} for Na–SL preheated at 770 or 970 K. The range of peaks can be deconvoluted into three peaks as shown in Fig. 1c and 1d, and definite peaks were observed at ca. 400 K (B-peak) and at ca. 470 K (C-peak). In these profiles, A-peak and B-peak were not separated. However, the temperature at the beginning of desorption from Na–SL was similar to that for A-peak in profiles (a) and (b), and at the initial stage of desorption from Na–SL preheated at 770 K (c), peak intensity increased quite steeply compared with the profile for Na–SL preheated at 970 K (d) although the shape of B-peak in both of the profiles (c) and (d) is estimated to be nearly identical. Thus, A-peak probably overlaps in the profile for Na–SL. The constants of the functions used for approximation of A- and C-peaks were similar to those for profiles (a) and (b) except for peak intensities.

Infrared Spectra of Adsorbed Methanol

To elucidate the adsorption sites of methanol, we recorded IR spectra of CD_3OD adsorbed on Na–SL preheated at 970 K. As shown in Fig. 2a, we can see some absorption bands after adsorption of CD_3OD at 390 K followed by evacuation at room temperature. The bands at 2245, 2145, and 2079 cm^{-1} are assigned to C–D stretching vibration in methoxyl group and the band at 2677 cm is assigned to O–D stretching vibration (*14, 15*). After evacuation at 430 K, the band at 2677 cm^{-1} had disappeared and broad absorption band at 2400–2800 cm^{-1} remained as shown in Fig. 2b, while the inten-

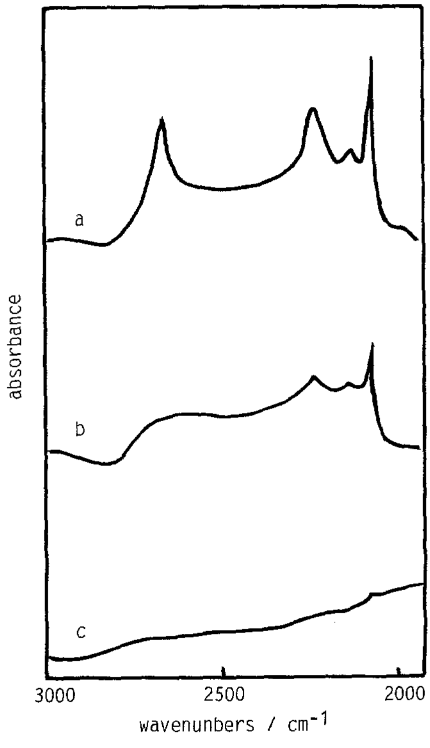

FIG. 2. IR absorption band of methanol adsorbed on Na–SL preheated at 970 K. (a) Evacuated at RT, (b) at 430 K, (c) at 770 K.

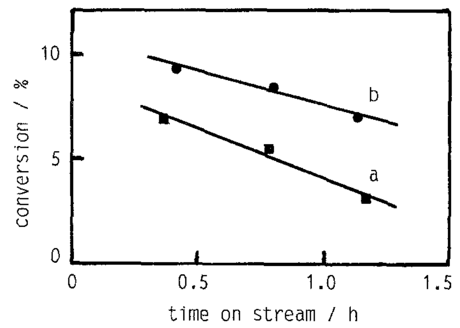

FIG. 3. Methanol dehydrogenation over Na–SL. (a) Na–SL, 770 K; (b) Na–SL, 970 K.

sity of the bands for OCD_3 group became weak. These absorption bands had almost disappeared after evacuation at 770 K as shown in Fig. 2c. It was expected that in the range above 3000 cm^{-1} the band of the internal hydroxyl groups in silicalite-1 is present; however, the band was not observed in these spectra of Na–SL probably because a considerable number of the internal hydroxyl groups were removed after evacuation at 970 K and because there were many noise peaks in this range under the experimental conditions. No appreciable change was observed in this range even after eliminating the noise signals by subtraction of the spectrum of Na–SL heated at 970 K from that of Na–SL adsorbing CD_3OD.

Methanol Conversion

As shown in Fig. 1, the preheating temperature of the silicalite samples affected the property for methanol adsorption. In general, catalytic activity relates seriously to adsorption property; therefore, the catalytic activity of Na–SL and SL would change with preheating temperatures. The catalytic activity of Na–SL preheated at 970 K was higher than that of Na–SL preheated at 770 K (Fig. 3) although the catalytic activity of Na–SL decreased with the time lapse of the reaction as reported previously (*2, 3*). Selectivity to formaldehyde was above 96%. When Na–SL was preheated at 1070 K, the crystal form changed to cristobalite and no catalytic activity was observed. No reaction was observed over SL preheated at 770 or 970 K.

MODELS AND MOLECULAR ORBITAL CALCULATIONS

It is known that a molecule with electron lone pairs interacts quite strongly with a cation of small radius on silica and zeolite surface (*16*). Hence, silanol groups and sodium ions in silicalite-1 are expected as adsorption sites for methanol. To estimate heat of methanol adsorption on these sites, we carried out ab initio molecular orbital calculations for the model compounds shown in Fig. 4. The geometrical data for methanol are experimental values and those for $(HO)_3SiOH$ and $(HO)_3SiONa$ are given in Table 1. Only the distance between methanol and its adsorption site was optimized.

We carried out Hartree–Fock calculations with the basis set of 6-31G with the

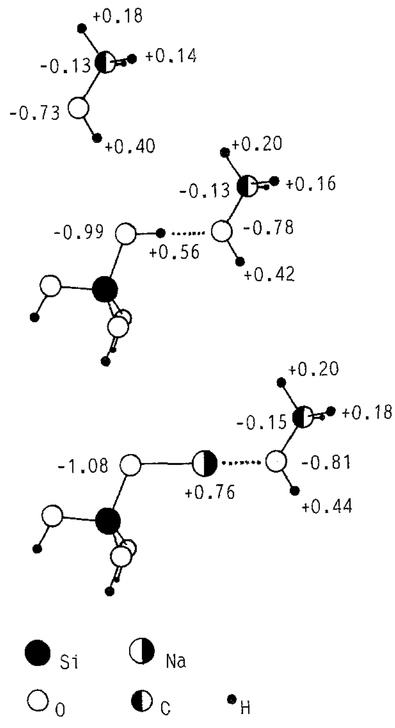

FIG. 4. Models and charge distribution of model compounds.

TABLE 1

Geometry of Model Compounds for Silicalite Surface

	Bond length (nm)		Bond angle (degree)
Si–O	0.163	O–Si–O	109.5
H–O	0.096	Si–O–H	115.0
Na–O	0.235	Si–O–Na	115.0

GAUSSIAN-86 program (*17*). It was confirmed that reliable stabilization energies can be calculated by using this calculation model and method in the case of small adsorbate on silicalite surface (*10*).

CALCULATION RESULTS

As represented in Table 2, stabilization energy between methanol and silanol group was calculated to be 41 kJ mol^{-1}. This stabilization results mainly from the hydrogen bonding between the oxygen atom in methanol and the hydrogen atom in silanol group. Senchenya *et al.* calculated the energies of hydrogen bonding between silanol and some adsorbates and confirmed that the hydrogen bonding between the oxygen atom in silanol and the hydrogen atom in an adsorbate is weaker than that between the oxygen atom in the adsorbate and the hydrogen atom in silanol (*18*). Hence, it is possible that the hydrogen atom in methanol interacts directly with the oxygen atom in the silanol group, but this hydrogen bonding is probably weak.

In the case of the interaction between methanol and a sodium ion, the stabilization energy was calculated to be 92 kJ mol^{-1}. As shown in Fig. 4, the presence of a sodium ion discernibly polarizes methanol as indicated by the charge distribution.

TABLE 2

Stabilization Energy of Model Compounds

Model	Stabilization energy (kJ mol^{-1})	Optimized distance (nm)
$(OH)_3SiOH–OHCH_3$	41	0.176
$(OH)_3SiONa–OHCH_3$	92	0.222

DISCUSSION

Silanol as Adsorption Site

As shown in Fig. 1, A-peak for SL preheated at 770 K was larger than that for SL preheated at 970 K. In the case of Na–SL, the tendency was the same. It is noteworthy that the number of hydroxyl groups in silicalite-1 preheated at 970 K is appreciably smaller than that in silicalite-1 preheated at 770 K and that the hydroxyl groups weakly adsorb ammonia (*9*). On the basis of the molecular orbital calculations, methanol is estimated to interact with silanol groups via hydrogen bonding. Thus, A-peak is believed to result from methanol molecules desorbed from the silanol sites in silicalite-1. We confirmed that silanol groups greater than 0.6 mmol g^{-1} are present in a sample of unmodified silicalite-1 preheated at 770 K (*11*), and this number is significantly larger than that of methanol causing A-peak (ca. 0.07 mmol g^{-1}). Flanigen *et al.* pointed out that the interaction between an adsorbate and the surface of silicalite channels is quite strong (*19*). Hence, we suppose that A-peak is related to the silanol site at a special position in a silicalite channel.

Sodium Ion as Adsorption Site

On the basis of the MO calculations, it is strongly suggested that a sodium ion in silicalite-1 is an adsorption site for methanol and adsorbs methanol more strongly than silanol does. It was confirmed that a molecule where high electron densities, e.g., electron lone pairs or π-bonds, are present is adsorbed on sodium ions in silicalite-1 (*9, 10*). In the TPD profiles for Na–SL we can see B-peak the size of which did not significantly change with the preheating temperatures, while no corresponding peak was observed in the profiles for SL. Hence, B-peak is related to the sodium ion site. Since B-peak in the TPD profile (Fig. 1d) for Na–SL preheated at 970 K was mainly disappeared at the desorption temperature of 430 K, the IR band at 2677 cm^{-1} in Fig. 2a is caused by the adsorption species responsible for B-peak in the TPD profile. Since the methanol OD stretching band was observed at ca. 2700 cm^{-1} (*14*), the band at 2677 cm^{-1} is probably due to OD in CD_3OD adsorbed on sodium ions.

Active Sites for Methanol Dehydrogenation

The IR bands for OD and OCD_3 groups in Fig. 2b are mainly associated with the adsorption species responsible for C-peak in the TPD profiles because these groups did not disappear after evacuation at 430 K. In the case of C_2D_5OD adsorption on silicalite-1, the IR bands for OD were observed at 2400–2700 cm^{-1} and 2762 cm^{-1} (*11*). The sharp band at 2762 cm^{-1} is due to the H–D exchange between the internal hydroxyl groups in silicalite-1 and C_2D_5OD, and the broadband at 2400–2700 cm^{-1} was concluded to be due to the silanol OD group interacting with the OC_2D_5 group, which are newly generated by the adsorption of C_2D_5OD (*11*). As shown in Fig. 2b and 2c, no sharp band at 2762 cm^{-1} was observed, suggesting that H–D exchange does not proceed in the adsorption of CD_3OD over Na–SL preheated at 970 K. We confirmed that the band at 2762 cm^{-1} observed in the case of C_2D_5OD adsorption does not disappear after heating at 770 K. This is reasonable because a considerable number of internal hydroxyl groups in silicalite-1 remains after heating at 770 K. On the other hand, the OD band at 2400–2800 cm^{-1} in Fig. 2b almost disappeared after evacuation at 770 K (see Fig. 2c); therefore, the OD band is not due to internal hydroxyl groups in silicalite-1 deuterated by H–D exchange with CD_3OD, but to the silanol newly generated by adsorption of CD_3OD on Na–SL. The adsorption sites for ethanol are probably some defects associated with Si–O–Si oxygen bridges generated by dehydration of the internal hydroxyl groups in silicalite-1, and the silanol and ethoxyl groups are generated by dissociative adsorption of ethanol with cleavage of the oxygen bridge, i.e., $C_2D_5OD + Si\text{–}O\text{–}Si^* \rightarrow Si\text{–}OC_2D_5 + DO\text{–}Si$ (*11*). This mechanism enables us to suppose that the OD and OCD_3 groups responsible for the absorption bands in Fig. 2b are generated by adsorption of CD_3OD on the defect mentioned above. The number of the defects in silicalite-1 increases with an increase of preheating temperatures in the range of 770–970 K because these defects are generated mainly by condensation of internal hydroxyl groups in silicalite-1 (*11*). Actually, the size of C-peak related to the preheating temperature of the sample as shown in Fig. 1; thus, we believe that methanol is adsorbed on the defects associated with oxygen bridges in silicalite-1 as well as ethanol and that these defects are responsible for C-peak. It is possible that CD_3O groups are formed by dehydration between CD_3OD and the residual hydroxyl groups on Na–SL followed by heating. However, we did not observe the change of IR spectra in the range above 3000 cm^{-1}. Hence, the number of CD_3O groups formed by the reaction with the hydroxyl groups is estimated to be quite small, if they exist. The defects described above are believed to catalyze ethanol dehydrogenation to acetaldehyde; the intermediates are hydroxyl and ethoxyl groups formed through dissociative ethanol adsorption on these oxygen bridges (*11*). Hence, methanol dehydrogenation would also be driven by these sites. As shown in Figs. 1c and 1d, the C-peak in the profile for Na–SL preheated at 970 K was larger than that in the profile for the sample preheated at 770 K. This finding is consistent with the results of methanol conversion that Na–SL preheated at 970 K exhibited higher activity than the sample preheated at 770 K. Thus, we propose that the active sites for methanol dehydrogenation in sodium-modified silicalite-1 are comprised of the defect oxygen bridges.

In the case of SL, no reaction occurred although discernible amounts of the defects are present (*11*); C-peak was observed in the profile for SL while it was significantly small compared with that for Na–SL. It was confirmed that the number of basic sites in sodium-modified silicalite-1 is very small; sodium ions in silicalite-1 are not present as NaOH or Na_2O because almost all carbon dioxide molecules adsorbed on sodium-modified silicalite-1 were removed at room temperature (*9*). Woolery *et al.* reported that a new broad IR band of hydroxyl groups at 3200–3600 cm^{-1} appeared after removal of sodium ions from silicalite-1 (*20*). Thus, sodium ions are probably replaced with hydrogen atoms in hydroxyl nests in silicalite-1. The quantum chemical study for $NaO–Si(OH)_3$ in Ref. (10) showed that the NaO group does not function as base or Lewis acid and that the interaction between the sodium ion and an adsorbate is mainly electrostatic, suggesting that sodium ion in silicalite-1 are not main active sites of methanol dehydrogenation. However, the catalytic activity toward methanol dehydrogenation depends on the amount of sodium ions in silicalite-1 (*3*). The reason is not clear and further elucidation is necessary, but we suppose the reason as follows. Sodium ions can be present near the defects associated with oxygen bridges because the bridges are mainly formed from the hydroxyl groups in the nests (*11*). As described in the previous section, sodium ions adsorb methanol molecules quite stably; hence, if sodium ions are present near the defects, the concentration of methanol around these bridges is considered to be very large and, as a result, sodium ions will assist methanol adsorption on the defects. Supposing that the adsorption process is quite slow and is a rate-determining step of methanol dehydrogenation, the reaction will proceed very well over sodium-modified silicalite-1 compared with sodium-unmodified silicalite-1. In the case of ethanol dehydrogenation, the rates of ethanol adsorption and desorption are estimated to be sufficiently fast because the reaction probably proceeds by the Langmuir–Hinshelwood mechanism (*11, 21*); hence, the heat of adsorption on the defect is more important than the rate of adsorption in the case of ethanol dehydrogenation, and sodium ions are not supposed to change the heat of adsorption of methanol or ethanol on the defects. It is noteworthy that Na–ZSM-5 (Si/Al = 95, Na/Al = 1.1 in molar ratio) catalyzed only methanol dehydration at 720 K and no hydrogen was detected in the present work, suggesting that sodium ions located outside the nests are not effective for methanol dehydrogenation.

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